Kinetics and Mechanism of Inversion at Asymmetric Nitrogen Centres in the Blue Copper(II) Complex of C-*rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane

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In order to investigate the effect of a co-ordinated ligand in the configurational conversion of a tetra-amine macrocyclic ligand complex of copper(II), the kinetics of the blue-to-red interconversion of the copper(II) complex of C-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (tet b) in the presence of monodentate ligands has been examined at 25 °C by using spectrophotometric techniques. The main pathway of this reaction is *via* a base which is co-ordinated to the metal ion. The co-ordinated base which contains another lone pair in the vicinity of the amine hydrogen catalyzes this reaction by partially removing the proton from nitrogen in the transition state. The reactivity order for the blue-to-red interconversion of blue[Cu(tet b)L]$^{(2-n)+}$ is blue[Cu(tet b)(OH)]$^{+}$ > blue[Cu(tet b)-(NH_2NH_2)]$^{2+}$ > blue[Cu(tet b)(SH)]$^{+}$ > blue[Cu(tet b)(NH_2OH)]$^{2+}$ > blue[Cu(tet b)(O_2CMe)]$^{+}$ > blue[Cu(tet b)(NO_2)]$^{+}$ > blue[Cu(tet b)(NH_2CSNH_2)]$^{2+}$ > blue[Cu(tet b)(SO_3)] > blue[Cu(tet b)-(HPO_4)] > blue[Cu(tet b)(S_2O_3)] ≫ blue[Cu(tet b)(CN)]$^{+}$, blue[Cu(tet b)(NCS)]$^{+}$, blue[Cu(tet b)(N_3)]$^{+}$, blue[Cu(tet b)(NH_3)]$^{2+}$, blue[Cu(tet b)($C_6H_5NH_2$)]$^{2+}$, blue[Cu(tet b)(C_5H_5N)]$^{2+}$, blue[Cu(tet b)Cl]$^{+}$, blue[Cu(tet b)Br]$^{+}$, blue[Cu(tet b)I]$^{+}$. The bases that fail to catalyze this reaction are of three types: (1) very weak bases such as Cl^-, Br^-, and I^-; (2) those containing only one lone pair such as NH_3, C_5H_5N, and $C_6H_5NH_2$; and (3) those containing two or more lone pairs which are far away from each other such as N_3^-, NCS^-, and CN^-. For the bases containing at least two lone pairs which are close to each other, the rate of this reaction increases as the basicity of the base increases, and as the negative charge of the base decreases.

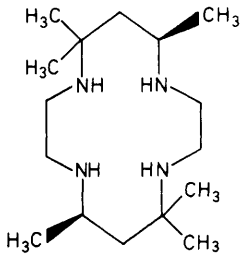
Since 1966, many transition-metal complexes containing open-chain amines have been resolved into their optical enantiomorphs, and the kinetics of inversions at asymmetric nitrogen centres in these complexes have been extensively studied.[1-16] These reactions are base-catalyzed, and the configurational inversions at nitrogen centres are expected only after deprotonation.[17] A free base-catalyzed mechanism was proposed for these reactions.[17]

The corresponding kinetics of inversion at asymmetric nitrogen centres in macrocyclic polyamine complexes have received very little attention.[18] Earlier work from this laboratory described the kinetics and mechanism of configurational conversions of tetra-amine macrocyclic ligand complexes of copper(II).[19,20] In marked contrast to the reactions of open-chain ligand complexes reported previously, the main reaction pathway of these reactions is *via* a hydroxide ion which is co-ordinated to the metal ion. A concerted co-ordinated base-catalyzed mechanism has been proposed in which intramolecular hydrogen bonding, nitrogen inversion, and ring conformation changes occur.[19] In order to investigate the effect of a co-ordinated ligand in the configurational conversion of a tetra-amine macrocyclic ligand complex of copper(II), we have investigated the kinetics of the inversion at asymmetric nitrogen centres in the blue copper(II) complex of C-*rac*-5,5,7,12,-12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (tet b) in the presence of monodentate ligands [equation (1)], and the results are reported herein.

$$\text{blue[Cu(tet b)]}^{2+} \xrightarrow{\text{base}} \text{red[Cu(tet b)]}^{2+} \qquad (1)$$

Experimental

Reagents.—Blue[Cu(tet b)][ClO_4]$_2$ was synthesized and purified by the same method as that reported previously.[21] The u.v. and visible spectra agreed quantitatively with reported values.[19] All other chemicals used were of GR grade (Merck or Fluka).



tet b

Instrumentation.—A Cary 17 spectrophotometer with a thermostatted cell compartment was used to measure absorption spectra and to follow the reaction. For pH measurements, a Radiometer PHM 64 equipped with a GK 2401 B combined electrode was used. The pH was standardized with National Bureau of Standards buffers, and the readings corrected to give the hydroxide-ion concentration. The hydroxide-ion concentration in 0.1 mol dm^{-3} $NaNO_3$ solution was calculated from $K_w = 10^{-13.78}$ and $-\log[H^+] = pH - 0.11$. The rate constants and stability constants were obtained by a linear least-squares fit of the data by using an Apple II minicomputer or a CDC Cyber-172 computer.

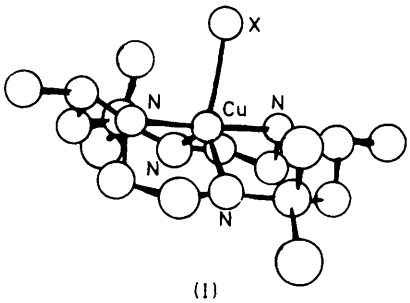
Equilibrium Constant Determinations.—The spectrophotometric measurements were carried out as described in previous papers.[19,22] The method of calculation was the same as described previously.[19,22]

Kinetic Measurements.—All reactions were measured at 840 nm and studied under conditions which were first order in the blue form of the copper complex. Plots of $\ln(A - A_\infty)$ *vs.* time were linear and gave the $k_{obs.}$ value reported. The A_∞ value for the absorbance was measured after 10 half-lives. A 10-cm cell was used. The mean percentage standard deviations for rate constants from individual runs are ±1% for $k_{obs.}$. The

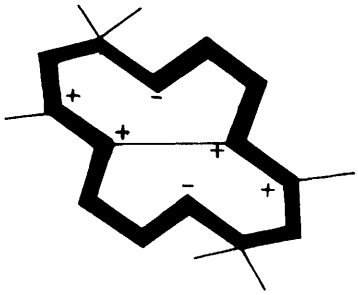
Table 1. Equilibrium constants for the reaction, blue[Cu(tet b)]$^{2+}$ + L^{n-} ⇌ blue[Cu(tet b)L]$^{(2-n)+}$, at 25.0 °C and I = 0.10 mol dm^{-3} ($NaNO_3$) [a]

L	K_L/dm^3 mol^{-1}
NH_3 [b]	23.3
C_5H_5N [b]	1.5
$C_6H_5NH_2$ [b]	4.8
NH_2CSNH_2 [b]	3.8
NH_2OH [c]	49.0
NH_2NH_2 [c]	27.9
SO_3^{2-} [d]	70.4
HPO_4^{2-} [d]	27.5
$S_2O_3^{2-}$ [d]	900

[a] Conditions: [Cu(tet b)$^{2+}$(blue)] = 5.11 × 10^{-4} mol dm^{-3}. [b] 8.0 × 10^{-2} mol dm^{-3} > [L] > 1.0 × 10^{-2} mol dm^{-3}. [c] 5.0 × 10^{-2} mol dm^{-3} > [L] > 1.0 × 10^{-2} mol dm^{-3}. [d] 5.0 × 10^{-2} mol dm^{-3} > [L] > 5.0 × 10^{-3} mol dm^{-3}.



(I)



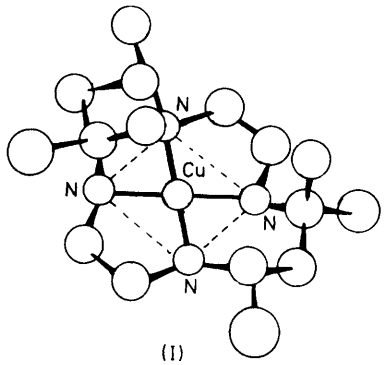
(II)

Figure 1. Crystal structure of blue[Cu(tet b)]$^{2+}$ and a representation of the configurations of the asymmetric centres and the conformations of the chelate rings of tet b in this complex. A plus sign at an asymmetric centre indicates that the hydrogen atom of the centre is above the plane of the macrocycle and a minus sign that it is below. *gauche* Conformations of the five-membered chelate rings and chair conformations of the six-membered chelate rings are indicated by heavier lines. The line shown in the representation is the fold axis

deviation of pH measurement is ±0.02 pH scale. Temperature control was maintained within ±0.1 °C. Ionic strength was controlled at 0.10 mol dm^{-3} by using $NaNO_3$.

Results

Addition of a solution of a monodentate ligand (L^{n-}) to an aqueous solution of blue[Cu(tet b)]$^{2+}$ resulted in the setting up of complex equilibria, involving the replacement of co-ordinated water by the monodentate ligand according to equation (2). The values of the equilibrium constants obtained by spectrophotometric methods are listed in Table 1.



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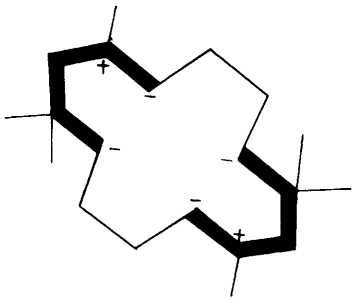

(II)

Figure 2. Structure of red[Cu(tet b)]$^{2+}$ and a representation of the configurations of the asymmetric centres and the conformations of the chelate rings of tet b in this complex, key as in Figure 1

$$\text{blue[Cu(tet b)]}^{2+} + L^{n-} \underset{}{\overset{K_L}{\rightleftharpoons}} \text{blue[Cu(tet b)L]}^{(2-n)+} \quad (2)$$

The red isomer of [Cu(tet b)]$^{2+}$ is much more stable than the blue species.[23] In basic solution blue[Cu(tet b)]$^{2+}$ converts slowly to the stable red isomer. All of the blue isomer converts to the red form under the conditions used in this study.[19,23] The observed first-order rate constants as a function of monodentate ligand concentration are given in Table 2.

Discussion

In this reaction structures have been determined for crystalline forms of the reactant [24] and of the product.[25] Therefore, it is possible to be quite specific about the rearrangements which accompany the colour change with [Cu(tet b)]$^{2+}$. The blue tet b complex has been isolated as [{Cu(tet b)}$_2$Cl][ClO_4]$_3$ which contains five-co-ordinate (trigonal-bipyramidal) copper as shown in Figure 1. This blue complex has the *RRRR*(*SSSS*) configuration of the chiral nitrogen centres which is normally seen in folded macrocyclic tetra-amine complexes.[26] The ligand is in its stable, folded configuration with both six-membered chelate rings in a symmetrical chair form and both five-membered chelate rings in a *gauche* form.[24] The chloride ion, which occupies one of the positions in the trigonal plane, dissociates from the copper in dilute solution but the electronic spectral characteristics of the complex in aqueous solution are similar to those of the crystals.[27] The structure of red[Cu(tet b)][ClO_4]$_2$ is shown in Figure 2. The copper is four-co-ordinate with a very slightly distorted square-planar arrangement of the four nitrogens of tet b. The six-membered chelate rings are in the chair form but the five-membered chelate rings are in an eclipsed (or partially eclipsed) form rather than the *gauche* form. This red species has the *RSRS*(*SRSR*) configuration of the chiral nitrogen centres which is also found in the most stable β-tet b complex with nickel(II).[26,28] The relative stabili-

Table 2. First-order rate constants for the blue-to-red interconversion of $[Cu(tet\ b)]^{2+}$ as a function of monodentate ligand concentration at 25.0 °C and I = 0.10 mol dm^{-3} ($NaNO_3$ + NaL) *

10^2[L]/ mol dm^{-3}	10^4[OH^-]/ mol dm^{-3}	$k_{obs.}$/s^{-1}
L = Cl^-		
0.00	3.31	9.70×10^{-4}
1.00	3.31	7.87×10^{-4}
2.00	3.31	7.04×10^{-4}
4.00	3.31	5.83×10^{-4}
6.00	3.31	4.32×10^{-4}
L = Br^-		
0.00	7.41	1.70×10^{-3}
1.00	7.41	1.43×10^{-3}
2.00	7.41	1.30×10^{-3}
4.00	7.41	1.12×10^{-3}
8.00	7.41	9.80×10^{-4}
L = I^-		
0.00	1.18	2.40×10^{-3}
1.00	1.18	1.96×10^{-3}
2.00	1.18	1.71×10^{-3}
4.00	1.18	1.42×10^{-3}
8.00	1.18	1.03×10^{-3}
L = NH_3		
0.00	2.24	6.45×10^{-4}
1.00	2.24	5.27×10^{-4}
2.00	2.24	4.80×10^{-4}
4.00	2.24	3.72×10^{-4}
8.00	2.24	3.41×10^{-4}
L = C_5H_5N		
0.00	2.29	7.10×10^{-4}
1.00	2.29	5.77×10^{-4}
2.00	2.29	5.67×10^{-4}
4.00	2.29	5.52×10^{-4}
8.00	2.29	5.24×10^{-4}
L = $C_6H_5NH_2$		
0.00	3.89	1.20×10^{-3}
1.00	3.89	1.11×10^{-3}
2.00	3.89	1.04×10^{-3}
4.00	3.89	9.70×10^{-4}
8.00	3.89	9.20×10^{-4}
L = N_3^-		
0.00	5.13	1.38×10^{-3}
2.00	5.13	1.14×10^{-3}
4.00	5.13	1.01×10^{-3}
6.00	5.13	9.13×10^{-3}
8.00	5.13	8.24×10^{-4}
L = NCS^-		
0.00	4.57	1.20×10^{-3}
0.250	4.57	7.32×10^{-4}
0.500	4.57	6.74×10^{-4}
1.00	4.57	5.80×10^{-4}
2.00	4.57	3.41×10^{-4}
L = CN^-		
0.00	2.95	8.80×10^{-4}
0.01	2.95	6.31×10^{-4}
0.02	2.95	2.10×10^{-4}
0.04	2.95	7.84×10^{-5}
0.08	2.95	1.38×10^{-5}
L = NH_2NH_2		
0.00	5.89	2.32×10^{-3}
1.25	5.89	1.21×10^{-3}
2.50	5.89	1.07×10^{-4}
5.00	5.89	8.94×10^{-4}
7.50	5.89	7.93×10^{-4}
L = NH_2OH		
0.00	3.39	8.36×10^{-4}
1.00	3.39	6.80×10^{-4}
2.00	3.39	5.54×10^{-4}
4.00	3.39	4.28×10^{-4}
8.00	3.39	3.09×10^{-4}
10.0	3.39	2.78×10^{-4}
L = NH_2CSNH_2		
0.00	5.75	1.47×10^{-3}
1.00	5.75	1.36×10^{-3}
2.00	5.75	1.32×10^{-3}
4.00	5.75	1.25×10^{-3}
8.00	5.75	1.13×10^{-3}
L = SH^-		
0.00	3.89	9.71×10^{-4}
0.20	3.89	8.82×10^{-4}
0.40	3.89	8.13×10^{-4}
0.60	3.89	7.74×10^{-4}
0.80	3.89	6.18×10^{-4}
L = O_2CMe^-		
0.00	2.04	6.48×10^{-4}
2.00	2.04	5.98×10^{-4}
4.00	2.04	5.46×10^{-4}
6.00	2.04	3.92×10^{-4}
8.00	2.04	2.45×10^{-4}
L = NO_2^-		
0.00	4.68	1.27×10^{-3}
2.00	4.68	1.02×10^{-3}
4.00	4.68	9.11×10^{-4}
6.00	4.68	7.28×10^{-4}
8.00	4.68	6.99×10^{-4}
L = SO_3^{2-}		
0.00	7.41	1.78×10^{-3}
1.00	7.41	1.76×10^{-3}
2.00	7.41	1.68×10^{-3}
4.00	7.41	1.31×10^{-3}
6.00	7.41	1.21×10^{-3}
L = HPO_4^{2-}		
0.00	2.40	3.31×10^{-3}
0.50	2.40	3.22×10^{-3}
1.00	2.40	3.02×10^{-3}
2.00	2.40	2.74×10^{-3}
4.00	2.40	2.29×10^{-3}
L = $S_2O_3^{2-}$		
0.00	1.91	5.04×10^{-4}
1.00	1.91	4.84×10^{-4}
2.00	1.91	4.70×10^{-4}
4.00	1.91	4.13×10^{-4}
6.00	1.91	3.31×10^{-4}

* Conditions: $[Cu(tet\ b)^{2+}(blue)]$ = 5.38×10^{-4} mol dm^{-3}; wavelength 840 nm.

ties of configurations of co-ordinated tet b have been discussed by Curtis and co-workers [26] and Warner and Busch.[28] The structures (I) and (II) in Figures 1 and 2 indicate the relative positions of the hydrogen atoms on the four nitrogens. It can be seen from these Figures that two of the four nitrogens must be inverted during the blue-to-red reaction.

Addition of the monodentate ligand, L^{n-}, to the solution of blue[Cu(tet b)]$^{2+}$ results in the rapid formation of blue[Cu(tet b)L]$^{(2-n)+}$ [equation (2)]. Some of the equilibrium constants of these reactions have been reported in previous papers,[19,22] and others measured in this work are given in Table 1. In the presence of CN^-, NCS^-, N_3^-, NH_3, $C_6H_5NH_2$, C_5H_5N, Cl^-, Br^-, or I^-, the rate of the blue-to-red interconversion is significantly smaller than that in the absence of these monodentate ligands as shown in Table 2. In the presence of NH_2NH_2, SH^-, NH_2OH, O_2CMe^-, NO_2^-, or NH_2CSNH_2, the rate constants are larger than those in the presence of halide or pseudohalide ions under the same conditions.

A reaction scheme consistent with these observations is given by equations (3)—(12).

$$\text{blue[Cu(tet b)]}^{2+} + L^{n-} \underset{}{\overset{K_L}{\rightleftharpoons}} \text{blue[Cu(tet b)L]}^{(2-n)+} \quad (3)$$

$$\text{blue[Cu(tet b)]}^{2+} + OH^- \overset{K_{OH}}{\rightleftharpoons} \text{blue[Cu(tet b)(OH)]}^{+} \quad (4)$$

$$\text{blue[Cu(tet b)L]}^{(2-n)+} \xrightarrow{k_L} \text{unstable[Cu(tet b)]}^{2+} + L^{n-} \quad (5)$$

$$\text{blue[Cu(tet b)(OH)]}^{+} \xrightarrow{k_{OH}} \text{unstable[Cu(tet b)]}^{2+} + OH^- \quad (6)$$

$$\text{unstable[Cu(tet b)]}^{2+} + L^{n-} \overset{K'_L}{\rightleftharpoons} \text{unstable[Cu(tet b)L]}^{(2-n)+} \quad (7)$$

$$\text{unstable[Cu(tet b)]}^{2+} + OH^- \overset{K'_{OH}}{\rightleftharpoons} \text{unstable[Cu(tet b)(OH)]}^{+} \quad (8)$$

$$\text{unstable[Cu(tet b)L]}^{(2-n)+} \xrightarrow{k'_L} \text{red[Cu(tet b)]}^{2+} + L^{n-} \quad (9)$$

$$\text{unstable[Cu(tet b)(OH)]}^{+} \xrightarrow{k'_{OH}} \text{red[Cu(tet b)]}^{2+} + OH^- \quad (10)$$

$$\text{red[Cu(tet b)]}^{2+} + L^{n-} \overset{K''_L}{\rightleftharpoons} \text{red[Cu(tet b)L]}^{(2-n)+} \quad (11)$$

$$\text{red[Cu(tet b)]}^{2+} + OH^- \overset{K''_{OH}}{\rightleftharpoons} \text{red[Cu(tet b)(OH)]}^{+} \quad (12)$$

The configuration of the unstable intermediate, unstable-[Cu(tet b)]$^{2+}$ is shown in Figure 3. As pointed out previously,[19] the inversion of the configuration of the first nitrogen, steps (5) and (6), is rate-determining. All the other steps are fast. The resulting rate expression is given by equation (13) where [Cu(tet b)(blue)]$_{total}$ refers to the sum [Cu(tet b)$^{2+}$(blue)] + [Cu(tet b)(OH)$^+$(blue)] + [Cu(tet b)L$^{(2-n)+}$(blue)].

$$d[\text{Cu(tet b)}^{2+}(\text{blue})]/dt = k_{obs.}[\text{Cu(tet b)(blue)}]_{total} = (k_{OH}K_{OH}[OH^-] + k_LK_L[L^{n-}])[\text{Cu(tet b)(blue)}]_{total}/(1 + K_{OH}[OH^-] + K_L[L^{n-}]) \quad (13)$$

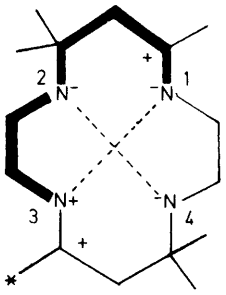

Figure 3. Configuration of [Cu(tet b)]$^{2+}$ after the inversion of N(1) and ring conformational changes to a tetrahedrally distorted square-planar structure. The axial C(7) methyl group is indicated with an asterisk, key as in Figure 1

Table 3. Equilibrium constants of adduct formation of [Cu(tet b)]$^{2+}$ with monodentate ligands and resolved rate constants of the blue-to-red interconversion of blue[Cu(tet b)L]$^{(2-n)+}$ at 25.0 °C and I = 0.10 mol dm^{-3} ($NaNO_3$ + NaL)

	K_L/dm^3 mol^{-1}		
L	spectrophotometric	kinetic	k_L/s^{-1}
Cl^-	15.5 [a]	15.4	[b]
Br^-	18.1 [a]	19.4	[b]
I^-	22.2 [a]	22.0	[b]
NH_3	23.3	21.3	[b]
C_5H_5N	1.5	1.4	[b]
$C_6H_5NH_2$	4.8	5.6	[b]
N_3^-	84.5 [a]	80.2	[b]
NCS^-	147 [a]	139	[b]
CN^-	2 950 [a]	2 900	[b]
NH_2NH_2	27.9	33.1	3.98×10^{-4}
NH_2OH	49.0	47.5	1.26×10^{-4}
NH_2CSNH_2	3.8	3.0	1.12×10^{-5}
SH^-	300 [a]	270	1.41×10^{-4}
O_2CMe^-	1.8 [a]	1.7	3.98×10^{-5}
NO_2^-	7.2 [a]	7.0	1.60×10^{-5}
SO_3^{2-}	70.4	74.2	3.50×10^{-7}
HPO_4^{2-}	27.5	25.1	1.36×10^{-7}
$S_2O_3^{2-}$	900	891	1.08×10^{-7}

[a] From ref. 22. [b] The value of the constant is zero or extremely small.

The values of K_{OH} and k_{OH} are 506 dm^3 mol^{-1} and 6.22×10^{-3} s^{-1} respectively.[19] The $k_{obs.}$ values given in Table 2 are equal to $(k_{OH}K_{OH}[OH^-] + k_LK_L[L^{n-}])/(1 + K_{OH}[OH^-] + K_L[L^{n-}])$. A plot of $k_{obs.}$ *vs.* $\{k_{OH}K_{OH}[OH^-] - k_{obs.}(1 + K_{OH}[OH^-])\}/[L^{n-}]$ gives a straight line with slope $1/K_L$ and intercept k_L for each of these monodentate ligands in accord with equation (14). The equilibrium constants, K_L, evaluated

$$k_{obs.} = (1/K_L)\{k_{OH}K_{OH}[OH^-] - k_{obs.}(1 + K_{OH}[OH^-])\}/[L^{n-}] + k_L \quad (14)$$

from the kinetic data by using equation (14) were in excellent agreement with those obtained by spectrophotometric measurements under equilibrium conditions as shown in Table 3. This agreement gives the convincing evidence that co-ordinated base provides the best pathway for the blue-to-red interconversion. Co-ordinated base which contains a lone pair in the vicinity of the amine hydrogen will catalyze the blue-to-red interconversion by partially removing the proton from nitrogen in the transition state. A pre-equilibrium

step with the formation of a low concentration of deprotonated nitrogen bonded to copper can be ruled out on the basis that the reaction depends on the source of the base and that the reaction is catalyzed not only by hydroxide ion but also by a lot of basic anions and undissociated bases.

The product, $k_L K_L$, can be used as a measure of the effectiveness of the base, L^{n-}, to catalyze this blue-to-red interconversion according to the relationship in equation (13). In general, the equilibrium constant, K_L, increases as the softness and the basicity of the base increase.[22] For bases with the same charge type, these equilibrium constants can be quantitatively correlated by the Edwards equation,[29] $\log(K/K_0) = \alpha E_n + \beta H$, where K_0 is the constant for a reference base (say, water), H is a proton basicity factor, and E_n is a redox factor.[30] The affinity of red[Cu(tet b)]$^{2+}$ for L is much less than that of the blue form.[22,29]

Several resolved rate constants, k_L, for the analogous blue-to-red interconversion of [Cu(tet a)L]$^{(2-n)+}$ have been reported.[20] These constants are much greater than the corresponding rate constants of the reactions of [Cu(tet b)L]$^{(2-n)+}$. These relative reactivities are mainly attributed to the relative stabilities of the chelate rings of these two complexes. The nitrogen which inverts in the reaction of blue[Cu(tet b)L]$^{(2-n)+}$ starts with a stable five-membered ring in a *gauche* form and a stable six-membered ring in a chair form.[24] On the other hand, the nitrogen which inverts in the reaction of blue[Cu(tet a)L]$^{(2-n)+}$ starts with an unstable eclipsed five-membered ring and an unstable skew-boat six-membered ring.[31,32]

The results listed in Table 3 indicate that the reactivity order for the blue-to-red interconversion of blue[Cu(tet b)L]$^{(2-n)+}$ is blue[Cu(tet b)(OH)]$^+$ > blue[Cu(tet b)(NH_2NH_2)]$^{2+}$ > blue[Cu(tet b)(SH)]$^+$ > blue[Cu(tet b)(NH_2OH)]$^{2+}$ > blue[Cu(tet b)(O_2CMe)]$^+$ > blue[Cu(tet b)(NO_2)]$^+$ > blue[Cu(tet b)(NH_2CSNH_2)]$^{2+}$ > blue[Cu(tet b)(SO_3)] > blue[Cu(tet b)(HPO_4)] > blue[Cu(tet b)(S_2O_3)] ≫ blue[Cu(tet b)(CN)]$^+$, blue[Cu(tet b)(NCS)]$^+$, blue[Cu(tet b)(N_3)]$^+$, blue[Cu(tet b)(NH_3)]$^{2+}$, blue[Cu(tet b)($C_6H_5NH_2$)]$^{2+}$, blue [Cu(tet b)(C_5H_5N)]$^{2+}$ blue[Cu(tet b)Cl]$^+$, blue[Cu(tet b)Br]$^+$, blue[Cu(tet b)I]$^+$. The values of k_L in Table 3 divide the bases into two classes, those which fail to catalyze the blue-to-red interconversion and those which have significant resolved rate constants. Those bases that fail to catalyze the blue-to-red interconversion are of three types: (1) very weak bases such as Cl^-, Br^-, and I^-; (2) those containing only one lone pair such as NH_3, pyridine, and aniline; and (3) those containing two or more lone pairs which are far away from each other such as N_3^-, NCS^-, and CN^-. These bases diminish the ability of the hydroxide ion to catalyze the interconversion reaction as shown in Table 2. This inhibition can be attributed to the formation of the unreactive five-co-ordinate complex blue[Cu(tet b)L]$^{(2-n)+}$, which prevents or reduces the extent of the formation of the reactive hydroxide-ion complex, blue-[Cu(tet b)(OH)]$^+$. Furthermore the spectrally measured equilibrium constants for blue[Cu(tet b)L]$^{(2-n)+}$ agree with those measured on the basis of the rate data and proposed mechanism as shown in Table 3. These agreements strongly support the co-ordinated base-catalyzed mechanism proposed for this reaction.

In studying base-catalyzed reactions, we must always be concerned with the question of whether the process is a specific free base-catalyzed, general free base-catalyzed or co-ordinated base-catalyzed one. The kinetic effect of the base containing only one lone pair can contribute significant insight into the reactions and might even be considered diagnostic of the mechanism. A reaction is said to be specific base-catalyzed when it is catalyzed by the hydroxide ion but not by undissociated bases. General base-catalysis is observed when all proton acceptors will catalyze a reaction by removing a proton from

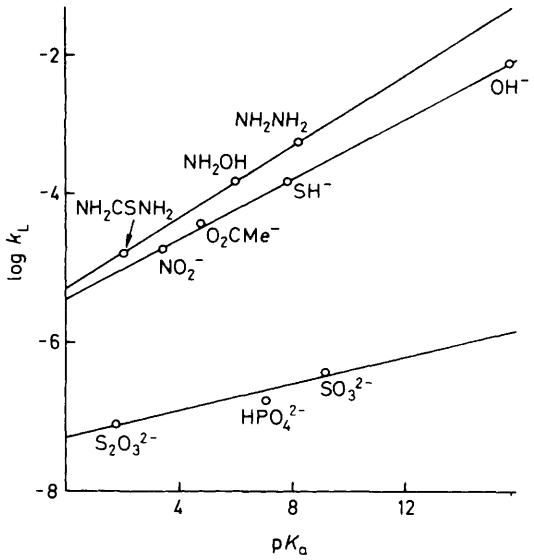

Figure 4. Plot of log k_L for the blue-to-red interconversion of [Cu(tet b)L]$^{(2-n)+}$ *vs.* pK_a for the base which contains at least two lone pairs in the vicinity of each other

the substrate in the transition state. Co-ordinated base-catalyzed reactions, on the other hand, are inhibited by bases containing only one lone pair. The bases, such as NH_3, C_5H_5N, and $C_6H_5NH_2$, have no mechanistic effect in a specific free base-catalyzed reaction, accelerate a general free base-catalyzed reaction, but inhibit a co-ordinated base-catalyzed reaction

The most striking feature of a co-ordinated base-catalyzed reaction is the requirements of the base. In addition to basicity, the base which accelerates a co-ordinated base-catalyzed reaction contains at least two lone pairs that are close to each other. In contrast, the bases, such as NH_3, $C_6H_5NH_2$, and C_5H_5N, which contain only one lone pair, and the bases, such as N_3^-, NCS^-, and CN^-, which contain two or more lone pairs that are far away from each other fail to catalyze the blue-to-red interconversion. The trend for the bases which contain at least two lone pairs in the vicinity of each other, I^-, Br^-, Cl^-, $S_2O_3^{2-}$ < HPO_4^{2-} < SO_3^{2-} < NH_2CSNH_2 < NO_2^- < O_2CMe^- < NH_2OH < SH^- < NH_2NH_2 < OH^-, indicates that the reactivity of blue[Cu(tet b)L]$^{(2-n)+}$ is significantly influenced by the basicity and the charge type of the base. The basicity of the co-ordinated base is not known, and the basicity of the free base is taken as a reference. Plotting the basicity constant of the base which contains at least two lone pairs in the vicinity of each other defined as $\log[HL^{(1-n)+}]/([H^+][L^{n-}])$ or pK_a as abscissa and log k_L as ordinate, we obtain a Brönsted relationship for the bases with the same charge type as shown in Figure 4. From this Figure, it is clear that the value of k_L increases as the basicity of the base increases, and as the negative charge of the base decreases. The significant charge effect suggests that solvation of the complex may play an important role in the concerted blue-to-red interconversion of blue[Cu(tet b)L]$^{(2-n)+}$, in which intramolecular hydrogen bonding, nitrogen inversion, and ring conformational changes occur.

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